

PROCESS AND APPARATUS TO REDUCE THE AMOUNTS OF ARSENIC IN WATER

FIELD OF THE INVENTION

This invention generally is directed to a process and apparatus to reduce the amounts of arsenic in water and, more particularly, to reduce the amounts of arsenic in drinking water in home, rural or relatively smaller drinking water systems, by contacting arsenic-containing water with a reactant, such as limestone, dolomite, clay materials including zeolite, iron oxide, magnesium carbonate, mixtures or combinations thereof, or similar compositions.

BACKGROUND OF THE INVENTION

Arsenic is a persistent, bio-accumulative toxin. At a pH of 8 and above, arsenic is readily soluble and thus transports easily through surface and ground water. The United States government drinking water standard for arsenic currently is 50 parts per billion, but is expected to be significantly lowered in the near future due to its toxicity and possible links to cancer. One proposal under consideration would set the federal water standard as low as 5 parts per billion.

Current arsenic remediation technologies are relatively expensive, require substantial technical equipment and trained personnel to achieve significant reductions in arsenic levels and are generally unsuitable for individual users, rural communities or relatively smaller water systems. Lowering the federal water standard for arsenic would place significantly increased economic and other pressures on those water systems that would be required to meet lower standard for arsenic.

According to estimates by the United States Environmental Protection Agency, a water standard of 5 parts per billion arsenic would cost consumers \$374 million per year. In another estimate, the American Water Works Association has estimated a minimum cost of \$1.4 billion per

year, along with an initial capitalization cost of \$14 billion, to meet the proposed 5 parts per billion standard. An estimated 6,600 water systems nationwide serving at least 22.5 million people would be required to upgrade their existing systems to meet the proposed 5 parts per billion standard.

5 If the proposed 5 parts per billion federal drinking water standard for arsenic becomes effective, many water systems will be in immediate danger of being out of compliance. For example, the South Dakota Department of Environment and Natural Resources estimates that 65 (18.6%) of that state's public water systems would violate a drinking water standard for arsenic of 5 parts per billion. Although larger community water treatment plants in more populous states may be able to meet the proposed federal water standard with existing technology and personnel, smaller water
10 systems and other water systems with limited financial and technical resources may not be capable of doing so. For example, such smaller and other water systems may include individual wells, rural communities, tribal water treatment facilities, urban communities with smaller populations (such as less than 10,000 people), urban communities lacking financial and technical resources to use existing technologies and individuals desiring on-site arsenic removal regardless of water source.

15 The need for a low cost, efficient arsenic removal system for such water systems is not unique to the United States. In many places throughout the world, excessive arsenic in potable water is a critical health issue, regardless of existing or non-existing regulations. The World Health Organization has compiled reports of relatively high levels of arsenic in drinking water in many countries, including Mexico, China and Bangladesh.

20 Current remediation technologies commonly considered for removal or reduction of the amounts of arsenic in potable water include ion exchange, coagulation and filtration, activated

alumina, lime softening, various iron based media and reverse osmosis. Each of these have significant shortcomings.

For example, ion exchange technology currently is used to remove or reduce the amounts of certain contaminants, including arsenic, in water. In an ion exchange system, the surface of a bed of resin beads contains negative charges, which are neutralized, and positive charges, which then pick up the negatively charged arsenic. However, existing ion exchange resins do not selectively attract only arsenic, but also attract other contaminants, such as sulfate, selenium, fluoride, nitrate and dissolved solids. As such, the efficiency of arsenic removal or reduction is not optimized. Also, suspended solids and iron precipitation may clog the system. In any event, an ion exchange system must eventually be regenerated, typically by flushing with brine. This results in a concentrated brine solution containing high levels of arsenic and other contaminants, which in turn creates a waste disposal issue. Further, an ion exchange system does not provide an indication of the level of arsenic in the bed or of the bed being saturated with arsenic. Moreover, an ion exchange system is too expensive, inefficient and complex for use in smaller water systems or as an end use application, such as a home, farm, business or individual well.

Coagulation and filtration is a batch process involving segregating a fixed amount of arsenic-containing water into a tank, adding iron to coagulate the arsenic, and filtering the batch to remove the coagulated arsenic. This process requires significant capital equipment and trained personnel and is most efficient at a mid-range pH. As a non-continuous process that is relatively expensive and complex, coagulation and filtration also is unsuitable for smaller water systems or as an end use application.

Both ion exchange technology and coagulation and filtration have been shown to reduce arsenic in water to about 2 parts per billion. However, both techniques are more effective when arsenic is in the form of As(V). If As(III) is present, it must first be oxidized to As(V), which adds a pretreatment step, greater costs and greater technical resources of equipment and personnel. One also must attend to the disposal of the resulting arsenic-contaminated sludge.

Lime softening is a process in which highly trained personnel adjust the pH of the arsenic-containing water to a relatively high pH, which facilitates the adsorption of arsenic onto larger particles, such as iron hydroxide, and then reduce the remaining water to a potable pH level. As with the ion exchange and the coagulation and filtration technologies, lime softening creates a waste product that creates disposal issues, is relatively expensive, requires trained personnel to operate the equipment and is not a continuous process.

Activated alumina, reverse osmosis and a variety of other technologies utilizing iron-based media are other processes that are currently considered for removal or reduction of arsenic in drinking water. Activated alumina requires significant technical intervention and processing, making it impractical for all but larger water systems. Reverse osmosis is not an effective process for this purpose, since up to 80-90 % of the water is discarded. Iron-based media generally involves the use of iron oxide, e.g., sand coated with rust, to attract, remove and hold arsenic from the water. These processes generally have significant problems with capacity, water quality, efficiency and waste disposal.

Therefore, a need exists for a process and apparatus to reduce the amounts of arsenic in water, particularly with less expense, less complexity, less personnel requirements and less waste disposal issues. With arsenic levels in drinking water increasingly becoming a health concern in the

United States and elsewhere and with a possible significant reduction in the federal water standard for arsenic in drinking water, this need is particularly acute for home, individual, rural and relatively smaller drinking water systems.

BRIEF DESCRIPTION OF THE DRAWINGS

5 Figure 1 is a schematic depicting one embodiment of an apparatus and process to reduce the amounts of arsenic in drinking water.

Figure 2 is a schematic depicting another embodiment of an apparatus and process to reduce the amounts of arsenic in drinking water.

10 Figure 3 is a schematic depicting another embodiment of an apparatus and process to reduce the amounts of arsenic in drinking water.

Figure 4 is a graph depicting adsorption of arsenic by limestone.

Figure 5 is a graph depicting the pH of arsenic-containing water and the adsorption of arsenic.

DETAILED DESCRIPTION OF THE INVENTION

15 This invention generally is directed to a process and apparatus to reduce the amounts of arsenic in water and, more particularly, to reduce the amounts of arsenic in drinking water in home, rural or relatively smaller drinking water systems, by contacting the arsenic-containing water with a reactant, such as limestone, dolomite, clay materials including zeolite, iron oxide, magnesium carbonate, mixtures or combinations thereof, or similar compositions. As described more fully below, the present invention may be advantageously employed at the source of the water, at the point
20 of use of the water, or at points between the source and the user to reduce even relatively high

amounts of arsenic. For example, employing crushed limestone in the present invention has reduced arsenic levels in a sample of water from 100 parts per billion to less than 5 parts per billion in a matter of minutes. The present invention has the additional advantage of low cost disposal of a relatively stable and benign waste product that may be suitable for ordinary landfills.

5 In one embodiment of the invention, water containing arsenic is placed in contact with a reactant, such as limestone, dolomite, clay materials including zeolite, iron oxide, magnesium carbonate, mixtures or combinations thereof, or similar compositions. Arsenic is removed from the water, for example, by precipitation or absorption. When limestone is used as the reactant, it is believed that arsenic is removed from the water by the precipitation of calcium carbonate on the surface of the limestone. The level of arsenic in the water is reduced, preferably to below approximately 30 parts per billion, more preferably to below approximately 20 parts per billion, even more preferably to below approximately 10 parts per billion and most preferably to below approximately 5 parts per billion.

10 The arsenic-containing water may be from any source of water, including surface and underground sources and may be used for water directed to any water system or user, including large water treatment systems, rural or smaller water systems, or individual users. The relative simplicity of the present invention reduces the cost and technical requirements of conventional arsenic mediation techniques, which makes it particularly useful for individual users, rural communities or relatively smaller water systems. The present invention may be employed at the point of the source of the water, at the point of use by the end user, or at any point between the source and the user. The water may contain arsenic in levels considered to be unhealthy for human consumption or use, e.g., up to 100 ppb arsenic and higher.

The reactant employed to reduce the amount of arsenic in the water may be limestone, dolomite, clay materials such as zeolites, iron oxide, magnesium carbonate, mixtures or combinations thereof, and similar compositions. Limestone and dolomite are similar compounds and the terms are sometimes used interchangeably. As used herein, limestone is considered to be primarily calcium carbonate and dolomite is considered to be primarily calcium carbonate, with some magnesium carbonate. Limestone and dolomite are common minerals found in many parts of the world, including the United States. They are readily available and relatively inexpensive, particularly in the quantities utilized in the present invention. In general, limestone or dolomite is preferred over the other materials due to their widespread availability, relatively low cost, ease of forming into a variety of configurations and ease of use. Limestone is generally preferred over dolomite due to its greater availability. In some areas, dolomite may be preferred due to availability in that particular geographic area. Clay materials, such as zeolites, may also be used, but generally must be mined, are more expensive and are less preferred. Mixtures and combinations of these materials alternatively may be employed.

The reactant may be used in a variety of forms, including the natural or raw material form, broken into smaller pieces, crushed to a specified size or formed into pellets, blocks or other shapes. The reactant also may be sintered, which typically increases its hardness and porosity. In general, smaller pieces have greater surface area and therefore greater sites in which the reactant may react with the arsenic. The preferred size, shape and other characteristics of the reactant depend in part on the particular application, as set forth more fully below.

Contacting the arsenic-containing water with the reactant may be accomplished in a variety of ways. For example, arsenic-containing water may be passed in a substantially continuous flow

through a filter containing the reactant. As shown in Figure 1, the arsenic-containing water may be introduced into filter system 10 through inlet 16, passed in a substantially continuous flow through cartridge 14 containing the reactant and removed from the filter system 10 through outlet 18. The filter system 10 preferably comprises a housing 12 to hold the cartridge 19 containing the reactant, particularly in a point of use application utilizing a filter system. When the reactant is in need of replacement, the cartridge 14 may be supplied with additional or replacement reactant or preferably the cartridge 14 may be removed and replaced with another cartridge containing fresh reactant. A filter system 10 for a point of use application preferably would be sufficiently compact to be installed within the house or building, more preferably under the sink or otherwise near the faucet. For such applications, the housing 12 and cartridge 19 preferably would be approximately 2 to 3 feet in length and approximately 3 to 6 inches in diameter and be configured to contain approximately 10 to 15 pounds of reactant.

In a filter system application, the preferred size, shape and other characteristics of the reactant generally depends on the desired flow rate of water, the level of arsenic contamination, the reactant used and other factors. In general, as the size of the reactant particles become smaller, the flow rates of the water through the filter decreases, eventually allowing insufficient or even no water to flow through the filter. On the other hand, as the size of the reactant particles become larger, the number of potential reaction sites decreases and the efficiency of the system decreases. In a filter system application for an individual user, the limestone or dolomite is preferably crushed or ground, preferably to approximately 0.001 mm to approximately 7 mm in diameter, more preferably to approximately 0.001 mm to approximately 2 mm in diameter, and most preferably to approximately 0.001 mm to approximately 1 mm in diameter. Alternatively, the limestone or dolomite may formed

into pellets, preferably approximately 5 mm to approximately 7 mm in diameter. As the volume of water to be treated increases, the amount of reactant to be used also increases, with the reactant preferably ground as fine as practicable.

In another embodiment of the present invention, the arsenic-containing water may be passed through a packed column containing the reactant. As shown in Figure 2, arsenic-containing water is introduced through inlet **32** into packed column **34** containing the reactant **36**. The water passes through the packed column of reactant **36**, which reduces the amounts of arsenic in the water, and exits the packed column **34** through outlet **38**.

The preferred size and characteristics of the column depends upon the end use application. For a single household, the column may be small enough to fit under the sink or large enough to treat all of the household water. Generally, the size of any particular unit is a function of the desired water effluent flow rate, the acceptable pressure drop and the desired length of time for the reactant in the column to be in service. A column system has an advantage over a reservoir system in that the effluent water is treated and usable up until the time of arsenic breakthrough, which occurs when the arsenic concentration in the effluent water reaches an undesirable level. At that point, the packed column reactant material is nearly saturated with arsenic compounds. The column may then be removed and replaced with another column containing fresh reactant. Preferably, the reactant is packed into the column so as minimize water bypassing the reactant and to minimize escape of the reactant into the effluent water. For example, the reactant may be packed in a gradient of sizes or with different particle sizes, e.g., with the smallest particles in the middle of the column and the largest sizes towards the outside. Inert materials, such as sand, or active materials, such as activated

carbon, may also be used in the column ends to retain the fine reactant particles. Screens or filters may also be used to retain the reactant particles.

In an application utilizing a packed column, the preferred size, shape and other characteristics of the reactant will depend on the desired flow rate of water, the allowable pressure drop, the desired velocity of water through the column, the level of arsenic contamination, the reactant used and other factors. Again, as the size of the particles become smaller, the flow rates of the water through the packed column generally decreases, eventually allowing insufficient or even no water to flow through. On the other hand, as the size of the particles become larger, there is a decreased number of potential reaction sites and the efficiency of the system decreases. In a packed column application, the reactant is preferably crushed or ground and classified to approximately 0.001 mm to approximately 10 mm in diameter, more preferably to approximately 0.001 mm to approximately 1 mm in diameter, and most preferably to approximately 0.001 mm to approximately 0.1 mm in diameter. Alternatively, the reactant may be formed into pellets, preferably approximately 0.1 mm to approximately 10 mm nominal diameter/length and more preferably approximately 1 mm to approximately 5 mm nominal diameter/length. As the volume of water to be treated increases, the amount of reactant to be used increases and the reactant preferably is crushed to a relatively smaller particle size.

In yet another embodiment of the invention, arsenic-containing water may be treated within a reservoir, including a reservoir used as storage. As shown in Figure 3, in a reservoir treatment system 50, arsenic-containing water is introduced through inlet 52 into reservoir 54. Reactant 57 is placed into reservoir 54 such that the arsenic-containing water comes in contact with at least a portion of the reactant 57 before exiting through outlet 58. The reservoir 54 may be anything that

is capable of holding a volume of water, such as a well, a tank or a tower. Water in relatively small reservoirs, such as individual water bottles or containers, may also be treated by placing the reactant into an enclosure, such as a tea bag, that is adapted to allow direct contact between the reactant and the water when the enclosure is inserted into the reservoir. The reactant 57 may be placed in contact with the arsenic-containing water in any number of ways, including placing and mixing the reactant 57 directly into the water, inserting into the arsenic-containing water a container, such as a bag with a porous membrane or a cage-like box that allows direct contact between the arsenic-containing water and the reactant 57 held within the container, or by positioning the reactant 57 in proximity to the outlet of the reservoir. Alternative methods may include incorporating the reactant through materials processing techniques into a rigid, yet porous base or by incorporating the reactant as a surface coating on a rigid, porous media.

In an application where the reactant is inserted into a reservoir, the preferred form of the reactant depends in part on the apparatus employed to house the reactant. For example, a bag or other container comprising a porous membrane may contain reactant that is finely ground, crushed, coarsely broken into pieces, blocks, natural or simply in the form that is most readily available. The openings in the membrane are designed to be sufficiently large to allow water to pass through the membrane, but sufficiently small to contain the reactant. In this application, it is preferred to employ a reactant that is relatively finely ground, such as approximately 0.001 mm to approximately 1 mm in diameter, to provide a relatively large number of potential reaction sites for the arsenic. For example, a membrane composed of plastic or similar materials may be used to contain reactant ground to approximately 0.001 mm to approximately 1 mm in diameter. Larger openings in the membrane or in the sides of the container preferably would result in using correspondingly larger

size particles of reactant. In a simple form, a single block of reactant may be placed on a platform or in an open cage. Most preferred is reactant finely ground to submicron particle size and molded to form porous pellets approximately 5 mm to approximately 10 mm in diameter.

As an example, one may consider the case of a relatively small water treatment plant for approximately 250 to 300 homes that utilizes water from a well and stores it in a water tower. In such a system, one may employ the present invention in a variety of ways, including by distributing filter or packed column systems to each end user, installing a packed column at the effluent of the water tower, inserting the reactant into the water tower, as set forth above, or installing a packed column to treat the water before it is stored in the water tower. In this case of a relatively small water treatment plant, it is generally preferred to either distribute filter reactant systems to each end user or to install a packed column to treat the water before it is stored in the water tower. Alternatively, by providing each end user with a packed column reactant system, the end user may preferentially treat only the water that needs to be treated. This will lower the expense to the end user, who may selectively treat only water to be used for human consumption and not treat water for other uses, such as for plants, the lawn, in toilets, etc.

Over time, the reactant will be consumed by its reaction with the arsenic in the water and will need to be replaced with fresh reactant. The length of time between such replacement of reactant will depend on a number of factors, including the volume of water treated, the amount of arsenic and other contaminants in the water and the amount, size, shape and type of reactant used, among other things. To determine the appropriate time to replace the reactant, the operator may regularly follow a proscribed schedule based on these factors, as provided by the supplier, or preferably test the water and/or the reactant to determine whether replacement of the reactant is necessary or desired.

Employing the present invention to treat even relatively large volumes of water with arsenic in amounts above drinking water standards produces a relatively small and compact amount of solid reactant with adsorbed arsenic. Because the arsenic is believed to be strongly bound to the reactant, arsenic is not expected to significantly leach out under normal waste disposal conditions. For example, using limestone as the reactant in the present invention generates an arsenic-laden waste limestone, which is relatively stable, even when subjected to the low pH (pH=2.88) environment of a Toxicity Characteristic Leaching Procedure Test.

Batch and column experiments indicate that the use of limestone in the present invention is capable of effectively reducing the amounts of arsenic in water from even relatively high levels to less than 5 parts per billion. For example, referring to Figure 4, a batch experiment was conducted with 100 mL water containing 109 parts per billion arsenic. Limestone in the form of 5 to 7 millimeter grain size was added in small increments to separate flasks, each containing 100 mL of water at 109 parts per billion arsenic. The flasks were agitated for 48 hours and the final arsenic concentration was measured. The results are shown in Figure 4, which indicates a marked reduction in arsenic concentrations (to 5 parts per billion or less) with relatively small amounts of limestone (40 to 100 grams).

In these experiments, limestone in all of the grain sizes tested, ranging from 0.001 mm to 7 mm in diameter, reduced arsenic concentrations from greater than 100 parts per billion to less than 5 parts per billion. In general, the arsenic removal process in these experiments was more efficient with smaller grain sizes of limestone and most efficient with the smallest grain sizes tested. Limestone successfully removed arsenic from standard solutions, regardless of the pH of the water, within the normal pH range of drinking water. For example, referring to Figure 5, 10 grams of 1 mm

to 2 mm limestone was added to 100 mL water containing approximately 100 parts per billion arsenic. The initial pH of the water was set at approximately $\frac{1}{2}$ pH units between approximately pH 4 and pH 10. The results are shown in Figure 5, which indicates a reduction of the arsenic concentration to approximately 10 parts per billion or less throughout the pH range tested. These experiments demonstrate that the present invention effectively reduces the amounts of arsenic in water throughout a relatively wide variance of pH, including the common, naturally occurring pH range of water.

While various embodiments of the present invention have been described in detail, it is apparent that modifications and adaptations of those embodiments will occur to those skilled in the art. However, it is to be expressly understood that such modifications and adaptations are within the spirit and scope of the present invention.